Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

"Statistically Representative Databases for Density Functional Theory via Data Science."

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Table S1: Basis sets used in the study. For more details, we refer the reader to the original publications, especially for the Minnesota Database.

Data-point	Basis set	Data-point	Basis set
All MGCDB84	def2-QZVPPD[1]	MN_MR-MGM-BE4_1	cc-pCVQZ (metal)[8] aug-cc-pCVQZ (non-metal)[9]
All GMTKN55	def2-QZVP[1]	MN_NHTBH38_10	MG3S[2]
MN_NCCE30_16	MG3S[2]	MN_NHTBH38_12	MG3S[2]
MN_PA8_2	MG3S[2]	MN_pTC13_13	MG3S[2]
MN_SR-MGN-BE107_76	MG3S[2]	MN_HC7_6	6-311+G(2df,2p)[10]
MN_NCCE30_8	MG3S[2]	MN_MR-MGM-BE4_3	cc-pCVQZ (metal)[8] aug-cc-pCVQZ (non-metal)[9]
MN_4pIsoE4_3	cc-pVQZ[3]	MN_IP23_14	cc-pVTZ-DK[4]
MN_MR-TM-BE13_13	aug-cc-pwCVTZ (metal)[4] aug-cc-pVTZ (non-metal)[5]	MN_AE17_6	cc-pCVQZ[9]
MN_IP23_20	cc-pVTZ-DK[6]	MN_MR-TM-BE13_12	aug-cc-pwCVTZ (metal)[4] aug-cc-pVTZ (non-metal)[5]
MN_SR-TM-BE17_1	def2-TZVP (metal) [1] ma-TZVP (non-metal)[1,7]	MN_MR-MGN-BE17_15	MG3S[2]
MN_SR-TM-BE17_9	def2-TZVP[1]	MN_MR-TMD-BE3_1	def2-TZVP[1]
MN_4dAEE5_4	cc-pVTZ-DK[6]	MN_MR-TMD-BE3_2	def2-TZVP[1]
MN_SR-MGN-BE107_43	MG3S[2]	MN_MR-TMD-BE3_3	def2-TZVP[1]
MN_ABDE13_6	ma-TZVP[1,7]	MN_SR-TM-BE17_7	def2-TZVP[1]
MN_MR-MGN-BE17_7	MG3S[2]	MN_SR-MGN-BE107_12	MG3S[2]
MN_HTBH38_3	MG3S[2]	MN_DC9_6	MG3S[2]
MN_SR-MGN-BE107_11	MG3S[2]		

Table S2: The 50 exchange-correlation functionals used in the analysis.

Name	Form	Explicit dispersion correction	Ref	Name	Form	Explicit dispersion correction	Ref
SVWN5	LSDA	None	11, 12	B3PW91	GH - GGA	None	13, 15, 39, 40
BP86	GGA	None	13, 14	B3LYP	GH - GGA	None	12, 13, 23, 39, 41,
PW91	GGA	None	15	B3LYP-D3(BJ)	GH - GGA	D3(BJ)	12, 13, 19, 23, 39, 41
B97-D	GGA	D3(0)[a]	16, 17	PBE0	GH - GGA	None	42
PBE	GGA	None	18	PBE0-D3(BJ)	GH - GGA	D3(BJ)	19, 42
PBE-D3(BJ)	GGA	D3(BJ)	18, 19	SOGGA11-X	GH - GGA	None	43
revPBE	GGA	None	20	B97-1	GH - GGA	None	44
revPBE-D3(BJ)	GGA	D3(BJ)	18, 19, 20	B97-2	GH - GGA	None	45
RPBE	GGA	None	18, 21	BMK	GH - mGGA	None	19, 46
HCTH/407	GGA	None	22	PW6B95	GH - mGGA	None	47
BLYP	GGA	None	13, 23	PW6B95-D3(BJ)	GH - mGGA	D3(BJ)	19, 47
OLYP	GGA	None	23, 24	M05	GH - mGGA	None	48
N12	NGA	None	25	M05-2X	GH - mGGA	None	49
SCAN-D3(BJ)	mGGA	D3(BJ)	19, 26	M06	GH - mGGA	None	50
B97M-V	mGGA	VV10	27, 28	M06-2X	GH - mGGA	None	50
B97M-rV	mGGA	rVV10	29, 30	M08-HX	GH - mGGA	None	51
τ-HCTH	mGGA	None	31	τ-HCTHh	GH - mGGA	None	31
TPSS	mGGA	None	32	TPSSh	GH - mGGA	None	52
revTPSS	mGGA	None	33	MN15	GH - mNGA	None	53
M06-L	mGGA	None	34	wB97X-V	RSH - GGA	VV10	38, 54
M06-L-D3(0)	mGGA	D3(0)	17, 34	N12-SX	RSH - NGA	None	55
M11-L	mGGA	None	35	wB97M-V	RSH - mGGA	VV10	28, 56
MN12-L	mNGA	None	36	HSE-HJS	RSH - mGGA	None	18, 57, 58
MN15-L	mNGA	None	37	M11	RSH - mGGA	None	59
HF		None	38	MN12-SX	RSH - mNGA	None	55

LSDA = Local Spin-Density Approximation; GGA = Generalized Gradient Approximation; NGA = Non-separable Gradient Approximation; mGGA = meta Generalized Gradient Approximation; mNGA = meta Non-separable Gradient Approximation; GH = Global Hybrid; RSH = Range-Separated Hybrid. The D3 correction is used in the original (0) and re-parametrized (BJ) version.

[a] In the original article, a slight modification of the D2 parameterization (S. Grimme, *J. Comput. Chem.*, **2004**, 1463–1473) was used.

Table S3 Mean Unsigned Errors (MUEs) used to generate the correlation plots in **Figure 1** of the main text. All values are in kcal/mol. See the previous table for the references of the functionals.

Functional	ASCDB MUE	All Data-points MUE	MGCDB84 MUE	GMTKN55 MUE	MN2015B MUE
B3LYP	15.26	3.41	2.61	5.07	6.58
B3PW91	10.29	3.07	2.61	3.89	5.32
B97-1	9.36	2.38	1.83	3.48	4.63
B97-2	11.47	3.12	2.60	4.23	5.05
B97-D	12.85	2.80	1.92	4.38	7.16
BLYP	18.27	4.69	3.85	6.49	7.90
BMK	7.35	2.35	2.07	2.44	5.00
BP86	14.25	4.63	3.74	5.65	10.89
HCTH/407	17.01	4.30	3.46	5.96	7.84
HSE-HJS	9.18	2.53	2.01	3.03	6.41
M05	8.30	2.46	2.03	3.09	5.00
M05-2X	8.65	1.89	1.41	2.43	5.37
M06	8.62	1.91	1.44	2.79	4.11
M06-2X	7.15	1.58	1.16	1.98	4.75
M06-L	13.36	2.59	1.82	4.43	5.14
M08-HX	7.76	1.63	1.22	1.91	5.17
M11	8.15	1.83	1.39	2.35	4.84
M11-L	13.15	3.03	2.40	4.35	5.56
MN12-L	8.37	2.49	2.06	3.05	5.31
MN12-SX	7.87	2.18	1.85	2.45	4.89
MN15	5.89	1.54	1.18	2.04	3.73
MN15-L	7.83	2.40	2.04	3.09	3.96
N12	9.78	3.77	3.20	4.47	7.50
N12-SX	7.79	2.56	2.12	3.16	5.23
OLYP	19.34	5.48	4.80	7.33	6.90
PBE	13.00	4.15	3.22	5.18	10.89
PBE0	9.10	2.55	2.02	3.02	6.65
PW6B95	8.00	2.49	1.99	2.45	7.93
PW91	12.46	3.92	2.98	5.20	9.79
revPBE	16.02	4.66	3.97	6.02	7.70
revTPSS	13.91	3.61	2.83	5.17	6.89
RPBE	16.76	4.61	3.85	6.07	7.99
SOGGA11-X	10.90	2.58	2.04	3.49	5.39
t-HCTH	15.13	3.93	3.12	5.65	7.02

t-HCTHhyb	9.82	2.71	2.15	3.80	5.20
TPSS	13.04	3.61	2.84	5.12	6.90
TPSSh	12.24	3.24	2.55	4.57	6.36
B97M-V	8.95	1.80	1.13	2.81	5.37
B97M-rV	8.82	1.78	1.12	2.79	5.42
wB97X-V	8.23	1.56	1.00	2.47	4.62
wB97M-V	5.62	1.19	0.71	1.83	4.49
B3LYP-D3(BJ)	8.75	2.01	1.37	2.90	6.03
PBE-D3(BJ)	13.30	3.93	2.90	5.03	11.35
PBE0-D3(BJ)	8.69	2.23	1.66	2.70	6.84
PW6B95-D3(BJ)	6.07	2.02	1.49	1.93	7.92
SCAN-D3(BJ)	8.50	2.56	1.94	3.39	6.56
SVWN5	42.59	13.04	9.51	13.83	47.87
HF	68.42	19.08	13.77	22.46	64.75
revPBE-D3(BJ)	10.11	2.91	2.21	3.96	7.00
M06-L-D3(0)	13.22	2.68	1.74	4.37	7.62

For a better visual representation, all data-points from the MGCDB84[60] database have a blue background. Instead, the data-points from GMTKN55[61] have a red background, and the Minnesota 2015B[62,63,64] data-points have a green background.

Table S4: Linear regression coefficients for MGCDB84.[60] The data-points not reported here have a zero coefficient.

MGCDB84 regression		Intercept	0.4159594
Data-point	**Coefficients**	**Data-point**	**Coefficients**
MGCDB84_AE18_7	0.0022507	MGCDB84_HAT707nonMR_466	0.0144524
MGCDB84_AlkAtom19_17	0.0081029	MGCDB84_PlatonicHD6_5	0.0040497
MGCDB84_Bauza30_9	0.0385295	MGCDB84_PlatonicIG6_4	0.0024323
MGCDB84_BH76RC_10	0.0340625	MGCDB84_S66x8_35	0.1704662
MGCDB84_BSR36_22	0.0246638	MGCDB84_S66x8_108	0.2310747
MGCDB84_FmH2O10_7	0.0105061	MGCDB84_TA13_6	0.0235536
MGCDB84_G21IP_28	0.0033971	MGCDB84_TAE140nonMR_4	0.0057926
MGCDB84_HAT707MR_484	0.0064691	MGCDB84_TAE140nonMR_78	0.0122523
MGCDB84_HAT707nonMR_194	0.0042939	MGCDB84_TAE140nonMR_120	0.0188418
MGCDB84_HAT707nonMR_219	0.0116288	MGCDB84_TAE140MR_132	0.0082053
MGCDB84_HAT707nonMR_302	0.0041668	MGCDB84_WATER27_23	0.0050195

Table S5 Mean Unsigned Errors (MUEs) and estimated MUEs (eMUEs) for the MGCDB84[60] database calculated using the coefficients reported in **table S4**, and used to generate **Figure 2** in the main text. All values are in kcal/mol.

MGCDB84					
Functionals	**MUE**	**eMUE**	**Functionals**	**MUE**	**eMUE**
B3LYP-D2[65,72-76]	1.57	1.61	**MS1-D3(0)**[113]	1.95	1.93
B3LYP-D3(BJ)[67,72-76]	1.37	1.37	**MS1**[113]	2.55	2.57
B3LYP-D3(CSO)[68,72-76]	1.32	1.32	**MS2-D3(0)**[113]	1.92	1.83
B3LYP-D3M(BJ)[69,72-76]	1.38	1.44	**MS2**[113]	2.28	2.22
B3LYP-D3(0)[66,72-76]	1.52	1.60	**MS2h-D3(0)** [113]	1.77	1.92
B3LYP[72-76]	2.61	2.59	**MS2h**[113]	2.16	2.32
B3LYP-NL[77]	1.51	1.65	**MVS**[115]	2.54	2.42
B3P86[72,73,75,78]	2.60	2.73	**MVSh**[115]	2.19	1.93
B3PW91-D2[65,73,78-80]	1.39	1.31	**MN12-L-D3(BJ)**[108]	1.92	1.83
B3PW91-D3(BJ)[67,73,78-80]	1.33	1.43	**MN12-L**[116]	2.06	2.05
B3PW91-D3(0)[66,73,78-80]	1.27	1.33	**MN12-SX-D3(BJ)**[108]	1.59	1.59
B3PW91[73,78-80]	2.61	2.63	**MN12-SX**[117]	1.85	1.90
B97-1-D2[81]	1.36	1.49	**MN15**[118]	1.18	1.18

B97-1[82]	1.83	1.89	**MN15-L**[119]	2.04	2.02
B97-2-D2[81]	1.21	1.16	**mPW91**[80,120]	3.25	3.26
B97-2[83]	2.60	2.65	**N12-D3(0)**[108]	2.36	2.32
B97-3-D2[81]	1.11	1.15	**N12**[121]	3.20	3.23
B97-3[84]	2.41	2.48	**N12-SX-D3(BJ)**[108]	1.76	1.81
B97-D2[85]	1.22	1.21	**N12-SX**[117]	2.12	2.10
B97-D3(BJ)[65,67]	1.87	1.83	**OLYP-D3(BJ)**[67,74,122]	2.33	2.49
B97-D3M(BJ)[65,69]	1.87	2.05	**OLYP-D3(0)**[66,74,122]	2.13	2.37
B97-D3(0)[65,66]	1.92	1.90	**OLYP**[74,122]	4.80	4.78
B97-D[65]	2.01	1.81	**oTPSS-D3(BJ)**[67,123]	1.80	1.64
B97[86]	2.28	2.32	**oTPSS-D3(0)**[123]	1.76	1.57
B97-K[87]	2.46	2.52	**PBE0-D2**[81]	1.78	1.82
B97M-rV[88]	1.12	1.10	**PBE0-D3(BJ)**[67,124]	1.66	1.72
B97M-V[89]	1.13	1.12	**PBE0-D3(CSO)**[68,124]	1.66	1.71
BLOC-D3(0)[90]	2.02	1.88	**PBE0-D3M(BJ)**[69,124]	1.69	1.76
BLOC[90]	2.98	2.87	**PBE0-D3(0)**[66,124]	1.69	1.76
BLYP-D2[65,73,74]	2.31	2.07	**PBE0**[124]	2.02	1.96
BLYP-D3(BJ)[67,73,74]	2.20	2.09	**PBE-D2**[65]	3.00	3.01
BLYP-D3(CSO)[68,73,74]	2.23	2.14	**PBE-D3(BJ)**[67,92]	2.90	2.95
BLYP-D3M(BJ)[69,73,74]	2.19	1.96	**PBE-D3(CSO)**[68,92]	2.87	2.91
BLYP-D3(0)[66,73,74]	2.30	2.24	**PBE-D3M(BJ)**[69,92]	2.92	2.98
BLYP[73,74]	3.85	3.78	**PBE-D3(0)**[66,92]	2.89	2.93
BLYP-NL[77]	2.46	2.33	**PBE**[92]	3.22	3.17
BMK-D2[81]	1.41	1.41	**PBEh-3c**[125]	4.02	4.12
BMK-D3(BJ)[67,87]	1.36	1.29	**PBEOP**[91,92]	3.70	3.54
BMK-D3(0)[66,87]	1.49	1.35	**PBEsol-D3(BJ)**[67,111]	5.35	5.10
BMK[87]	2.07	2.08	**PBEsol-D3(0)**[66,111]	5.43	5.23
BOP-D3(BJ)[73,91]	2.28	2.14	**PBEsol**[111]	5.42	4.80
BOP-D3(0) [73,91]	2.43	2.34	**PKZB**[126]	4.52	4.17
BOP[73,91]	4.84	4.67	**PW6B95-D2**[81]	1.43	1.24
BP86-D2[65,73,78]	2.85	2.75	**PW6B95-D3(BJ)**[67,127]	1.49	1.46
BP86-D3(BJ)[67,73,78]	2.75	2.81	**PW6B95-D3(CSO)**[68,127]	1.46	1.42
BP86-D3(CSO)[68,73,78]	2.75	2.85	**PW6B95-D3(0)**[66,127]	1.45	1.35
BP86-D3M(BJ)[69,73,78]	2.87	2.91	**PW6B95**[127]	1.99	1.95
BP86-D3(0)[66,73,78]	2.79	2.78	**PW91**[80]	2.98	2.99
BP86[73,78]	3.74	3.76	**PWB6K-D3(BJ)**[67,127]	1.95	1.91
BPBE-D3(BJ)[67,73,92]	2.33	2.35	**PWB6K-D3(0)**[66,127]	1.98	1.88
BPBE-D3(0)[66,73,92]	2.19	2.19	**PWB6K**[127]	2.18	2.12
BPBE[73,92]	3.88	3.98	**revPBE0-D3(BJ)**[67,92,124a,128]	1.63	1.83
CAM-B3LYP-D3(BJ)[67,93]	1.45	1.54	**revPBE0-D3(0)**[66,92,124a,128]	1.71	1.91

CAM-B3LYP-D3(0)[66,93]	1.59	1.72	**revPBE0**[92,124a,128]	3.25	3.43
CAM-B3LYP[93]	1.91	1.76	**revPBE-D2**[65,92,128]	2.27	2.14
GAM[94]	2.25	2.04	**revPBE-D3(BJ)** [67,92,128]	2.21	2.18
HCTH/120-D3(BJ)[67,95]	2.02	2.09	**revPBE-D3(0)**[66,92,128]	2.21	2.25
HCTH/120-D3(0)[66,95]	2.13	2.21	**revPBE**[92,128]	3.97	4.00
HCTH/120[95]	3.15	3.22	**revPBE-NL**[77]	2.44	2.38
HCTH/147[95]	3.53	3.62	**revTPSS**[129]	2.83	2.83
HCTH/407[96]	3.46	3.45	**revTPSSh**[130]	2.53	2.51
HCTH/93[82]	4.81	4.78	**RPBE-D3(BJ)**[67,92,131]	2.12	2.11
HF-D3(BJ)[67,97]	10.92	10.89	**RPBE-D3(0)**[66,92,131]	2.21	2.21
HF-D3(0)[66,97]	12.19	12.22	**RPBE**[92,131]	3.85	3.87
HF[97]	13.77	13.75	**rPW86PBE-D3(BJ)**[67,92,132]	2.79	2.43
HFLYP[74,97]	5.87	5.55	**rPW86PBE-D3(0)**[66,92,132]	2.87	2.56
HFPW92[79,97]	8.11	7.15	**rPW86PBE**[92,132]	3.40	3.05
HF-NL[77]	11.40	11.13	**rVV10**[71]	2.78	2.57
HSE-HJS-D3(BJ)[67,92,98,99]	1.63	1.68	**SCAN0**[133]	2.37	2.51
HSE-HJS-D3(0)[66,92,98,99]	1.67	1.72	**SCAN-D3(BJ)**[134]	1.94	2.02
HSE-HJS[92,98,99]	2.01	1.95	**SCAN-D3(0)**[134]	1.95	2.04
LC-VV10[70]	1.90	1.56	**SCAN**[135]	1.97	1.93
LC-ωPBE08-D3(BJ)[67,100]	1.73	1.38	**SCAN+rVV10**[136]	1.95	2.01
LC-ωPBE08-D3M(BJ)[69,100]	1.80	1.44	**SOGGA11-X-D3(BJ)**[108]	1.29	1.33
LC-ωPBE08-D3(0)[66,100]	1.73	1.35	**SOGGA11-X**[137]	2.04	2.12
LC-ωPBE08[100]	2.48	2.14	**SOGGA**[92,138]	5.68	4.90
LRC-ωPBE[101]	2.59	2.69	**SPW92**[79,139]	9.51	9.49
LRC-ωPBEh[101]	2.16	2.07	**SVWN5**[72,139]	9.51	9.49
M05-2X-D3(0)[66,102]	1.37	1.34	**τ-HCTH**[140]	3.12	3.08
M05-2X[102]	1.41	1.37	**τ-HCTHh**[140]	2.15	2.25
M05-D3(0)[66,103]	1.63	1.63	**TM**[141]	2.14	2.02
M05[103]	2.03	1.96	**TPSS-D2**[65,142]	2.14	2.10
M06-2X-D2[81]	1.16	1.17	**TPSS-D3(BJ)**[67,142]	1.99	2.08
M06-2X-D3(0)[66,104]	1.14	1.13	**TPSS-D3(CSO)**[68,142]	2.01	2.14
M06-2X[104]	1.16	1.21	**TPSS-D3(0)**[66,142]	2.00	2.03
M06-D2[81]	1.31	1.35	**TPSS**[142]	2.84	2.82
M06-D3(0)[66,104]	1.33	1.41	**TPSSh-D2**[81]	1.79	1.75
M06[104]	1.44	1.55	**TPSSh-D3(BJ)**[67,143]	1.66	1.77
M06-HF-D3(0)[66,105]	2.16	1.85	**TPSSh-D3(0)**[66,143]	1.70	1.74
M06-HF[105]	2.14	1.88	**TPSSh**[143]	2.55	2.53
M06-L-D2[81]	1.75	1.63	**VV10**[70]	2.80	2.60
M06-L-D3(0)[66,106]	1.74	1.71	**ωB97**[144]	1.47	1.42
M06-L[106]	1.82	1.81	**ωB97M-rV**[71,145]	0.72	0.80

M08-HX[107]	1.22	1.21	**ωB97M-V**[145]	0.71	0.79
M08-SO[107]	1.30	1.38	**ωB97X-D3**[146]	1.11	1.24
M11-D3(BJ)[108]	1.27	1.22	**ωB97X-D**[147]	1.08	1.24
M11[109]	1.39	1.35	**ωB97X**[144]	1.33	1.35
M11-L-D3(0)[108]	2.02	1.76	**ωB97X-rV**[71,148]	1.00	0.99
M11-L[110]	2.40	2.31	**ωB97X-V**[148]	1.00	0.98
mBEEF[111,112]	2.58	1.99	**ωM05-D**[149]	1.10	1.09
MS0-D3(0)[113]	2.23	2.34	**ωM06-D3**[146]	1.23	1.17
MS0[114]	2.35	2.41			

Table S6: Linear regression coefficients for GMTKN55.[61] The data-points not reported here have a zero coefficient.

GMTKN55 regression		**Intercept**	0.7364613
Data-point	**Coefficients**	**Data-point**	**Coefficients**
GMTKN55_BH76_45	0.0148906	GMTKN55_PCONF21_11	0.0573541
GMTKN55_DC13_2	0.0122999	GMTKN55_W4-11_7	0.0755413
GMTKN55_DC13_4	0.0227417	GMTKN55_W4-11_11	0.0169214
GMTKN55_ISOL24_4	0.0069133	GMTKN55_W4-11_34	0.0299297
GMTKN55_MB16-43_2	0.0148394	GMTKN55_W4-11_114	0.0217445
GMTKN55_MB16-43_5	0.0030353	GMTKN55_W4-11_115	0.0002151
GMTKN55_MB16-43_13	0.0043958	GMTKN55_W4-11_139	0.0101862
GMTKN55_MB16-43_28	0.0026937	GMTKN55_WATER27_14	0.0048557
GMTKN55_MB16-43_38	0.0054141	GMTKN55_WATER27_19	0.0186607
GMTKN55_MB16-43_40	0.0019886	GMTKN55_WCPT18_2	0.1183882

Table S7 Mean Unsigned Errors (MUEs) and estimated MUEs (eMUEs) for the GMTKN55[61] database calculated using the coefficients reported in **Table S6**, and used to generate **Figure 2** and **Figure 3** in the main text. All values are in kcal/mol.

GMTKN55					
Functionals	**MUE**	**eMUE**	**Functionals**	**MUE**	**eMUE**
APFD[150]	2.61	2.76	**MPW2PLYP-D3(0)**[66,167]	2.15	2.28
B1B95[151]	3.11	3.33	**MPW2PLYP-D3(BJ)**[61,167]	2.04	2.19
B1B95-D3(0)[66,151]	2.23	2.23	**MPWB1K**[165]	2.76	2.53
B1B95-D3(BJ)[151,152]	2.69	2.70	**MPWB1K-D3(0)**[66,165]	2.50	2.31
B1LYP[73,74,124,153]	5.73	5.60	**MPWB1K-D3(BJ)**[152,165]	2.62	2.49
B1LYP-D3(0)[66,73,74,124,153]	4.02	3.91	**MPWKCIS1K**[166]	3.69	3.62
B1LYP-D3(BJ)[61,73,74,124,153]	2.89	2.80	**MPWKCIS1K-D3(0)**[66,166]	2.74	2.68
B1P86[73,78,124]	3.62	3.73	**MPWKCIS1K-D3(BJ)**[61,166]	3.35	3.78
B1P86-D3(0)[66,73,78,124]	2.72	3.00	**mPWLYP**[74,120,153]	6.32	6.03
B1P86-D3(BJ)[61,73,78,124]	2.59	2.99	**mPWLYP-D3(0)**[66,74,120,153]	5.36	5.13
B2GPPLYP[154]	2.25	2.40	**mPWLYP-D3(BJ)** [74,120,152,153]	5.13	4.92
B2GPPLYP-D3(0)[66,154]	1.76	1.86	**mPWPW91**[120,168]	5.20	5.07
B2GPPLYP-D3(BJ)[61,154]	1.40	1.42	**mPWPW91-D3(0)**[66,120,168]	4.34	4.27
B2PLYP[155]	2.87	3.15	**mPWPW91-D3(BJ)**[61,120,168]	4.68	4.40
B2PLYP-D3(0)[66,155]	2.08	2.37	**N12**[121]	4.47	4.29
B2PLYP-D3(BJ)[152,155]	1.79	2.03	**N12-D3(0)**[108]	4.26	4.06
B3LYP[72-76]	5.07	4.98	**N12-SX**[117]	3.16	3.12
B3LYP-D3(0)[66,72-76]	3.50	3.45	**N12-SX-D3(BJ)**[108]	3.26	3.47
B3LYP-D3(BJ)[67,72-76]	2.90	2.90	**O3LYP**[169]	5.07	5.74
B3LYP-NL[77]	2.96	3.02	**O3LYP-D3(0)**[66,169]	4.63	5.14
B3P86[72,73,75,78]	3.90	4.09	**O3LYP-D3(BJ)**[61,169]	5.69	6.29
B3P86-D3(0)[66,72,73,75,78]	2.96	3.33	**OLYP**[74,122]	7.33	7.23
B3P86-D3(BJ)[61,72,73,75,78]	2.87	3.38	**OLYP-D3(0)**[66,74,122]	4.11	3.82
B3PW91[73,78-80]	3.89	3.91	**OLYP-D3(BJ)**[61,74,122]	4.36	4.06
B3PW91-D3(0)[66,73,78-80]	2.38	2.57	**OPBE**[92,122]	6.79	7.24
B3PW91-D3(BJ)[73,78-80,151]	2.47	2.61	**OPBE-D3(0)**[66,92,122]	5.02	4.96
B97-1[82]	3.48	3.45	**OPBE-D3(BJ)**[61,92,122]	6.09	6.57
B97-1-D3(0)[66,82]	2.72	2.72	**PBE**[92]	5.18	5.23
B97-1-D3(BJ)[61,82]	2.58	2.66	**PBE-D3(0)**[66,92]	4.89	4.89
B97-2[83]	4.23	4.31	**PBE-D3(BJ)**[67,92]	5.03	4.95
B97-2-D3(0)[66,83]	2.44	2.38	**PBE0**[124]	3.02	3.20
B97-2-D3(BJ)[61,83]	4.10	4.16	**PBE0-D3(0)**[66,124]	2.64	2.74
B97-D3-D3(0)[65,66]	4.38	4.27	**PBE0-D3(BJ)**[67,124]	2.70	2.77
B97-D3(BJ)[65,67]	4.03	4.07	**PBE1KCIS**[170]	3.58	3.69

B98[156]	3.70	3.49	**PBE1KCIS-D3(0)**[66,170]	3.09	3.13
B98-D3(0)[66,156]	2.65	2.45	**PBE1KCIS-D3(BJ)**[61,170]	3.75	4.16
B98-D3(BJ)[61,156]	2.55	2.57	**PBEh1PBE**[124,171]	3.01	3.12
BHLYP[157]	6.49	6.53	**PBEh1PBE-D3(0)**[66,124,171]	2.60	2.72
BHLYP-D3(0)[66,157]	5.31	5.33	**PBEh1PBE-D3(BJ)**[61,124,171]	2.96	3.24
BHLYP-D3(BJ)[152,157]	4.69	4.69	**PBEhPBE**[92,171]	5.09	5.11
BLYP[73,74]	6.49	6.53	**PBEhPBE-D3(0)**[66,92,171]	4.79	4.70
BLYP-D3(0)[66,73,74]	5.31	5.33	**PBEhPBE-D3(BJ)**[67,92,171]	5.23	5.04
BLYP-D3(BJ)[67,73,74]	4.69	4.69	**PKZB**[126]	5.90	6.17
BMK[87]	2.44	2.27	**PKZB-D3(0)**[66,126]	4.72	4.42
BMK-D3(0)[66,87]	2.31	2.69	**PW1PW**[124,168]	2.94	3.10
BMK-D3(BJ)[67,87]	2.60	2.94	**PW1PW-D3(0)**[61,124,168]	2.67	2.71
BP86[73,78]	5.65	5.73	**PW6B95**[127]	2.45	2.46
BP86-D3(0)[66,73,78]	4.62	4.86	**PW6B95-D3(0)**[66,127]	1.88	1.80
BP86-D3(BJ)[67,73,78]	4.75	4.88	**PW6B95-D3(BJ)**[67,127]	1.93	1.87
BPBE[73,92]	5.62	5.45	**PW91**[80]	5.20	5.33
BPBE-D3(0)[66,73,92]	4.01	3.83	**PW91-D3(BJ)**[67,80]	5.01	5.11
BPBE-D3(BJ)[67,73,92]	4.34	3.97	**PW91P86**[78,80]	5.96	6.43
DSD-BLYP[158]	2.20	2.48	**PW91P86-D3(0)**[66,78,80]	5.93	6.21
DSD-BLYP-D3(0)[66,158]	1.69	1.94	**PWPB95**[172]	1.89	2.28
DSD-BLYP-D3(BJ)[152,158]	1.29	1.41	**PWPB95-D3(0)**[66,172]	1.36	1.68
DSD-PBEB95[159]	1.66	2.15	**PWPB95-D3(BJ)**[152,172]	1.39	1.70
DSD-PBEB95-D3(BJ)[159]	1.24	1.59	**revPBE**[92,128]	6.02	5.98
DSD-PBEP86[160]	1.73	1.95	**revPBE-D3(0)**[66,92,128]	4.03	3.84
DSD-PBEP86-D3(BJ)[160]	1.29	1.40	**revPBE-D3(BJ)**[67,92,128]	3.96	3.89
HCTH[96]	5.96	5.94	**revTPSS**[129]	5.17	5.22
HCTH-D3(0)[66,96]	4.10	3.90	**revTPSS-D3(0)**[66,129]	4.28	4.29
HCTH-D3(BJ)[61,96]	5.99	6.13	**revTPSS-D3(BJ)**[67,129]	4.16	4.22
HISS[161]	3.36	3.01	**revTPSS0**[129,173]	4.71	4.84
HISS-D3(0)[66,161]	3.19	3.01	**revTPSS0-D3(0)**[66,129,173]	3.83	3.92
HISS-D3(BJ)[61,161]	3.43	3.62	**revTPSS0-D3(BJ)**[61,129,173]	3.47	3.56
HSE03[162]	3.14	3.10	**revTPSSh**[130]	4.71	4.78
HSE03-D3(0)[66,162]	2.78	2.72	**revTPSSh-D3(0)**[66,130]	3.79	3.80
HSE03-D3(BJ)[61,162]	3.11	3.25	**revTPSSh-D3(BJ)**[67,130]	3.48	3.51
HSE06[92,98,99]	3.03	3.15	**RPBE**[92,131]	6.07	6.08
HSE06-D3(0)[66,92,98,99]	2.67	2.83	**RPBE-D3(0)**[66,92,131]	4.12	3.89
HSE06-D3(BJ)[92,98,99,163]	2.59	2.77	**RPBE-D3(BJ)**[67,92,131]	4.99	4.99
LC-ωPBEh[164]	3.49	3.06	**rPW86PBE**[92,132]	5.41	5.26
LC-ωPBEh-D3(0)[66,164]	2.76	2.75	**rPW86PBE-D3(0)**[66,92,132]	4.66	4.57
LC-ωPBEh-D3(BJ)[61,164]	2.65	2.83	**rPW86PBE-D3(BJ)**[67,92,132]	4.50	4.41

M05[103]	3.09	3.17	**SCAN**[135]	3.36	3.24
M05-D3(0)[66,103]	2.60	2.66	**SCAN-D3(0)**[134]	3.35	3.17
M05-2X[102]	2.43	2.39	**SCAN-D3(BJ)**[134]	3.39	3.15
M05-2X-D3(0)[66,102]	2.44	2.41	**SOGGA11-X**[137]	3.49	3.41
M06[104]	2.79	2.88	**SOGGA11-X-D3(BJ)**[108]	2.23	2.42
M06-D3(0)[66,104]	2.67	2.77	**τ-HCTH**[140]	5.65	5.61
M06-L[106]	4.43	4.42	**τ-HCTH-D3(0)**[66,140]	4.21	4.07
M06-L-D3(0)[66,106]	4.37	4.37	**τ-HCTH-D3(BJ)**[61,140]	4.92	4.89
M06-2X[104]	1.98	2.03	**τ-HCTHh**[140]	3.80	3.72
M06-2X-D3(0)[66,104]	1.99	2.07	**τ-HCTHh-D3(0)**[66,140]	2.90	2.94
M08-HX[107]	1.91	2.10	**τ-HCTHh-D3(BJ)**[61,140]	3.12	3.13
M08-HX-D3(0)[66,107]	1.89	2.11	**TPSS**[142]	5.12	5.13
M11[109]	2.35	2.40	**TPSS-D3(0)**[66,142]	4.10	4.06
M11-D3(BJ)[108]	2.19	2.31	**TPSS-D3(BJ)**[67,142]	3.93	3.97
M11-L[110]	4.35	4.36	**TPSS0**[173]	4.60	4.63
M11-L-D3(0)[108]	3.76	3.58	**TPSS0-D3(0)**[66,173]	3.55	3.62
MN12-L[116]	3.05	2.84	**TPSS0-D3(BJ)**[67,173]	3.29	3.44
MN12-L-D3(BJ)[108]	3.12	2.95	**TPSS1KCIS**[174]	4.24	4.36
MN12-SX[117]	2.45	2.69	**TPSS1KCIS-D3(0)**[66,174]	3.01	2.97
MN12-SX-D3(BJ)[108]	2.20	2.46	**TPSS1KCIS-D3(BJ)**[61,174]	3.42	3.61
MN15[118]	2.04	2.20	**TPSSh**[143]	4.57	4.61
MN15-D3(BJ)[61,118]	2.04	2.20	**TPSSh-D3(0)**[66,143]	3.52	3.52
MN15-L[119]	3.09	3.05	**TPSSh-D3(BJ)**[143,152]	3.29	3.38
MN15L-D3(0)[61,119]	3.08	3.05	**VV10**[70]	4.45	4.41
MPW1B95[165]	2.41	2.45	**ωB97X-D3(0)**[146]	2.72	2.50
MPW1B95-D3(0)[66,165]	2.02	1.84	**ωB97X-V**[148]	2.47	2.45
MPW1B95-D3(BJ)[152,165]	2.16	2.11	**X3LYP**[175]	4.58	4.52
MPW1KCIS[166]	4.34	4.39	**X3LYP-D3(0)**[66,175]	3.51	3.41
MPW1KCIS-D3(0)[66,166]	3.25	3.26	**X3LYP-D3(BJ)**[61,175]	2.64	2.74
MPW1KCIS-D3(BJ)[61,166]	4.60	4.92	**XLYP**[74,175]	6.96	6.77
mPW1LYP[74,120,124,153]	4.87	4.73	**XLYP-D3(0)**[66,74,175]	5.20	4.95
mPW1LYP-D3(0)[61,74,120,124,153]	3.73	3.46	**XLYP-D3(BJ)**[61,74,175]	4.61	4.16
mPW1PW91[120,124,153]	3.46	3.31	**B97M-V**[89]	2.81	2.29
mPW1PW91-D3(0)[66,120,124,153]	2.50	2.49	**ωB97M-V**[145]	1.83	1.91
mPW1PW91-D3(BJ)[61,120,124,153]	2.57	2.66	**SVWN5**[72,139]	13.83	13.90
MPW2PLYP[167]	2.60	2.78	**HF**[97]	22.46	22.35

Table S8: Linear regression coefficients for Minnesota 2015B.[62,63,64] The data-points not reported here have a zero coefficient.

Minnesota 2015B regression		Intercept	2.3968004
Data-point	**Coefficients**	**Data-point**	**Coefficients**
MN_SR-MGN-BE107_11	0.0055525	MN_MR-TM-BE13_12	0.0028237
MN_SR-MGN-BE107_43	0.1637088	MN_MR-TMD-BE3_1	0.0044447
MN_SR-MGN-BE107_76	0.0985072	MN_MR-TMD-BE3_3	0.0038915
MN_ABDE13_6	0.1119293	MN_HC7_6	0.0089449
MN_MR-MGN-BE17_7	0.2089518	MN_AE17_6	0.0762471
MN_SR-TM-BE17_9	0.0111902	MN_DC9_6	0.0052714

Table S9 Mean Unsigned Errors (MUEs) and estimated MUEs (eMUEs) for the Minnesota 2015B[62,63,64] database calculated using the coefficients reported in **Table S8**, and used to generate **Figure 2** in the main text. All values are in kcal/mol.

Minnesota 2015B					
Functionals	**MUE**	**eMUE**	**Functionals**	**MUE**	**eMUE**
B3LYP[72-76]	6.58	6.10	**PBE**[92]	10.89	11.41
B3PW91[73,78-80]	5.32	5.14	**PBE0**[124]	6.65	6.61
B97-1[82]	4.63	4.99	**PW6B95**[127]	7.93	7.46
B97-2[83]	5.05	4.85	**PW91**[80]	9.79	10.01
B97-D3(0)[65,66]	7.16	6.43	**revPBE**[92,128]	7.70	8.05
BLYP[73,74]	7.9	7.10	**revTPSS**[129]	6.89	6.56
BMK[87]	5.00	5.07	**RPBE**[92,131]	7.99	9.09
BP86[73,78]	10.89	10.98	**SOGGA11-X**[137]	5.39	5.05
HCTH/407[96]	7.84	7.25	**τ-HCTH**[140]	7.02	6.50
HSE-HJS[92,98,99]	6.41	6.61	**τ-HCTHh**[140]	5.2	5.52
M05[103]	5.00	5.58	**TPSS**[142]	6.9	7.17
M05-2X[102]	5.37	5.32	**TPSSh**[143]	6.36	6.27
M06[104]	4.11	4.45	**B97M-V**[89]	5.37	5.62
M06-2X[104]	4.75	4.97	**B97M-rV**[88]	5.42	5.62
M06-L[106]	5.14	4.89	**ωB97X-V**[148]	4.62	4.80
M08-HX[107]	5.17	5.45	**ωB97M-V**[145]	4.49	4.04
M11[109]	4.84	5.30	**B3LYP-D3(BJ)**[67,72-78]	6.03	5.90
M11-L[110]	5.56	6.03	**PBE-D3(BJ)**[67,92]	11.35	11.78
MN12-L[116]	5.31	5.04	**PBE0-D3(BJ)**[67,124]	6.84	6.41
MN12-SX[117]	4.89	4.41	**PW6B95-D3(BJ)**[67,127]	7.92	7.27

MN15[118]	3.73	3.52	**SCAN-D3(BJ)**[134]	6.56	6.38
MN15-L[119]	3.96	5.19	**SVWN5**[72.139]	47.87	47.91
N12[121]	7.50	7.45	**HF**[97]	64.75	64.44
N12-SX[117]	5.23	5.38	**revPBE-D3(BJ)**[67,92,128]	7.00	6.91
OLYP[74,122]	6.90	6.79	**M06-L-D3(0)**[66,106]	7.62	7.72

Table S10: Regression coefficients used to generate the data in **Table S11** and the following **Figures S1-S3**. These coefficients have been obtained using the results reported in **Figure 27** and in the Supporting Information of Ref. 60.

Subset	Datapoint	Coefficient	Intercept
NCED	MGCDB84_NBC10_78	-0.195871	0.1854212
	MGCDB84_S22_15	0.2886815	
	MGCDB84_S66x8_35	0.134704	
	MGCDB84_S66x8_108	0.4420212	
	MGCDB84_3B-69-DIM_109	0.0553564	
NCEC	MGCDB84_3B-69-TRIM_27	0.3197298	0.2145383
	MGCDB84_3B-69-TRIM_47	0.0879081	
	MGCDB84_FmH2O10_7	0.0754265	
	MGCDB84_H2O20Bind4_2	0.0411903	
	MGCDB84_H2O20Bind10_10	0.0962495	
	MGCDB84_Shields38_12	0.5376574	
	MGCDB84_SW49Bind345_31	-0.082606	
	MGCDB84_WATER27_23	0.0508039	
NCD	MGCDB84_Bauza30_9	0.2867486	0.6117074
	MGCDB84_TA13_6	0.1325971	
IE	MGCDB84_Butanediol65_5	0.1992592	0.0651619
	MGCDB84_H2O16Rel5_2	0.1194496	
	MGCDB84_YMPJ519_122	1.0494281	
	MGCDB84_YMPJ519_465	0.4946946	
ID	MGCDB84_C20C24_8	0.0944638	1.9563859
	MGCDB84_ISOMERIZATION20_18	0.303692	
	MGCDB84_Styrene45_16	-0.258186	
BH	MGCDB84_NHTBH38_9	0.5525822	0.861731

	MGCDB84_NHTBH38_38	1.1207338	
TCE	MGCDB84_AlkAtom19_17	0.073346	1.7031688
	MGCDB84_IP13_2	0.0742135	
	MGCDB84_BDE99nonMR_75	0.1254814	
	MGCDB84_HAT707nonMR_194	0.1449713	
	MGCDB84_TAE140nonMR_4	0.0636813	
	MGCDB84_TAE140nonMR_36	0.1284973	
	MGCDB84_TAE140nonMR_41	0.0404557	
	MGCDB84_TAE140nonMR_77	0.009994	
	MGCDB84_TAE140nonMR_78	0.0773947	
	MGCDB84_TAE140nonMR_100	0.0105573	
	MGCDB84_TAE140nonMR_120	0.0278387	
	MGCDB84_BSR36_15	0.0213203	
TCD	MGCDB84_PlatonicTAE6_2	0.0657511	1.9610099
	MGCDB84_PlatonicTAE6_5	-0.032466	
	MGCDB84_PlatonicTAE6_6	0.0674866	
	MGCDB84_PlatonicIG6_4	0.0418479	
	MGCDB84_PlatonicIG6_6	0.0234373	
	MGCDB84_PlatonicHD6_6	0.0497696	
	MGCDB84_BDE99MR_4	0.1291813	
	MGCDB84_HAT707MR_349	-0.213672	
	MGCDB84_HAT707MR_513	0.1098048	
	MGCDB84_TAE140MR_132	0.1090816	

Also, please note that the results in **Table 2** represent a weighted average of the results reported below. The weights are obtained based on the number of data-points for each group of properties in MGCDB84, with the exclusion of the Barrier Heights group. **Figures S1-S3** have been generated using the results shown in the table below (**Table S11**).

Table S11 Estimated Root-Mean Square Errors (RMSEs) for three functionals and basis sets for the different groups of properties in the MGCDB84 (ref. 60) database. All data are in kcal/mol.

Functional:	Basis set:	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH
PBE-D3(BJ)	6-31G*[176]	2.22	46.49	1.74	0.98	3.61	12.64	20.55	8.26
	def2-SVPD[1]	0.98	6.53	1.00	1.11	1.42	11.41	22.17	10.35
	def2-TZVPPD[1]	0.56	6.05	1.32	0.73	5.66	9.84	18.12	10.14
B3LYP-D3(BJ)	6-31G*[176]	2.25	41.27	1.21	1.03	4.22	5.93	7.99	5.02
	def2-SVPD[1]	1.35	10.73	0.65	0.72	4.13	5.03	12.95	7.78
	def2-TZVPPD[1]	0.42	3.31	0.63	0.40	6.61	3.78	6.31	6.75
ωB97M-V	6-31G*[176]	4.85	55.08	0.86	2.38	4.49	11.11	19.15	2.80
	def2-SVPD[1]	1.34	8.52	0.80	0.63	3.37	7.16	17.20	4.09
	def2-TZVPPD[1]	0.21	0.84	0.85	0.23	2.26	2.63	3.40	3.56

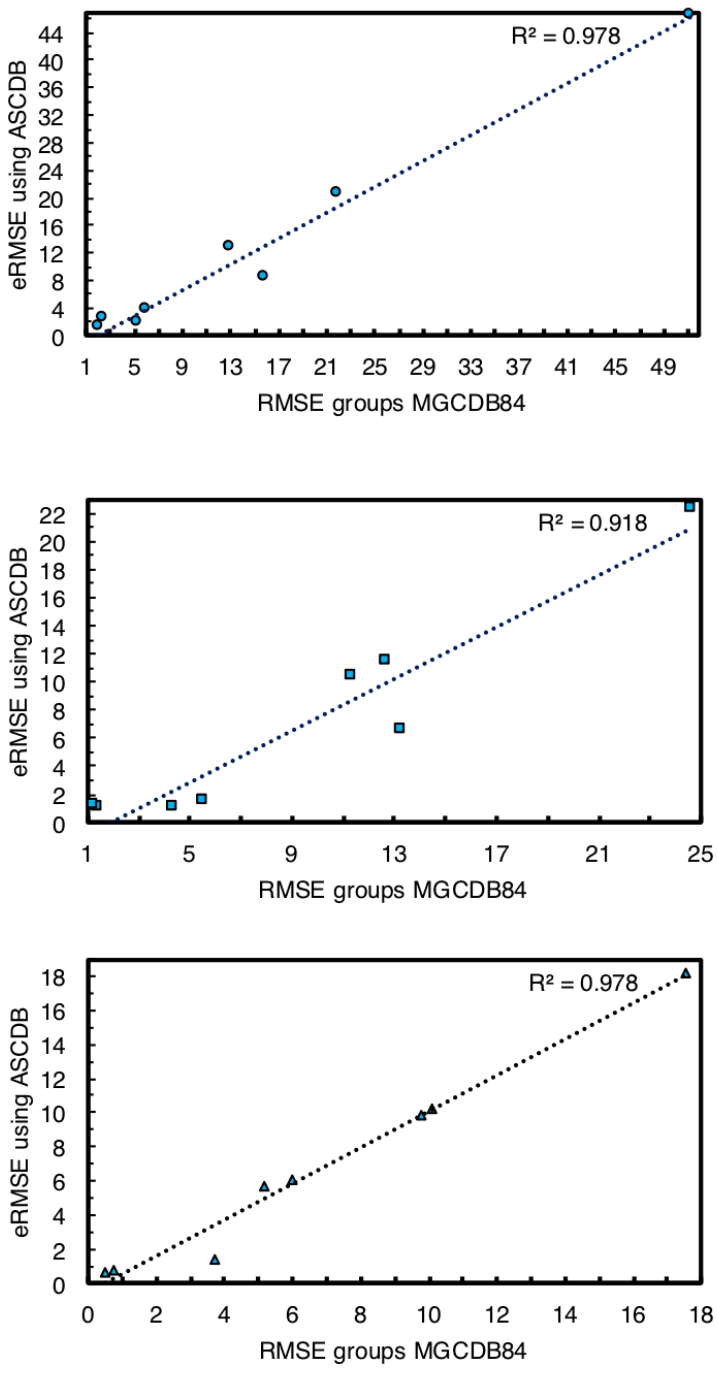

Figure S1 Calculated MUEs and estimated MUEs for PBE-D3(BJ) with three basis sets: 6-31G* (blue dots), def2-SVPD (blue squares), and def2-TZVPPD (blue triangles). Units on the axis are kcal/mol.

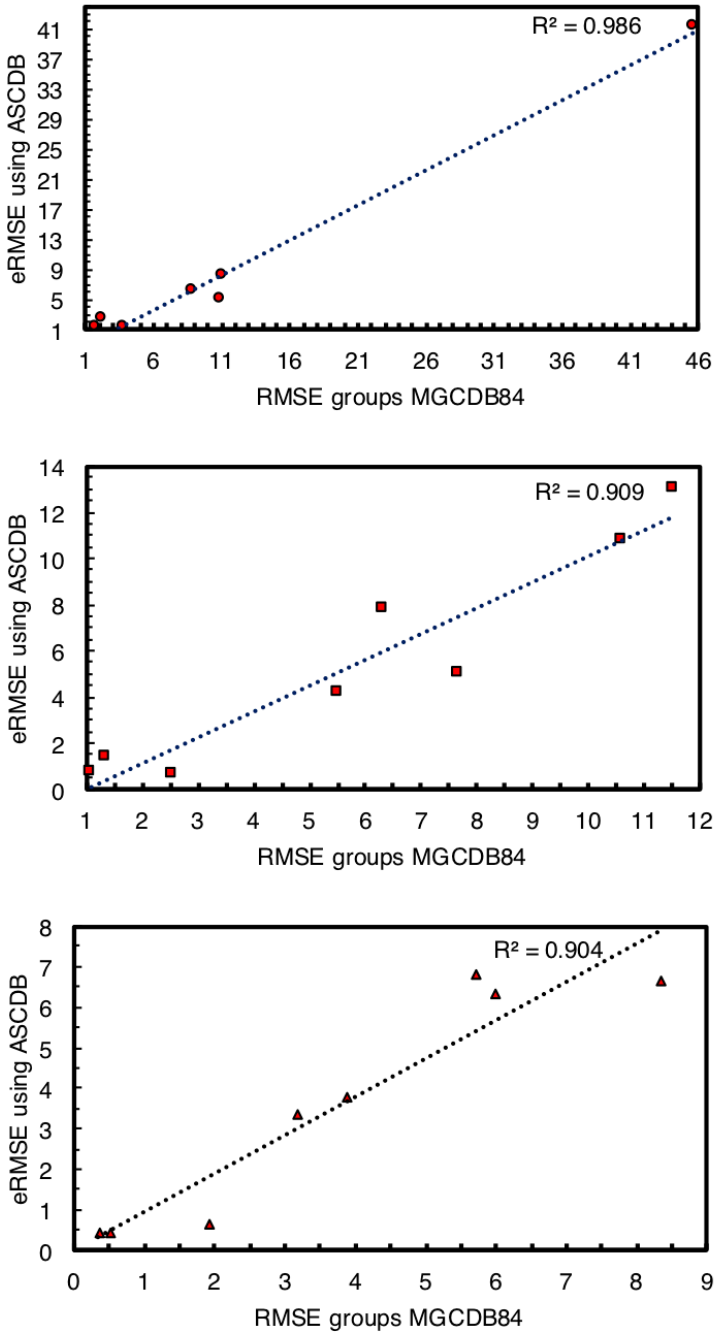

Figure S2 Calculated MUEs plotted against estimated MUEs (eMUEs) for the B3LYP-D3(BJ) functional with three basis sets: 6-31G* (red dots), def2-SVPD (red squares), and def2-TZVPPD (red triangles). Units on the axis are kcal/mol.

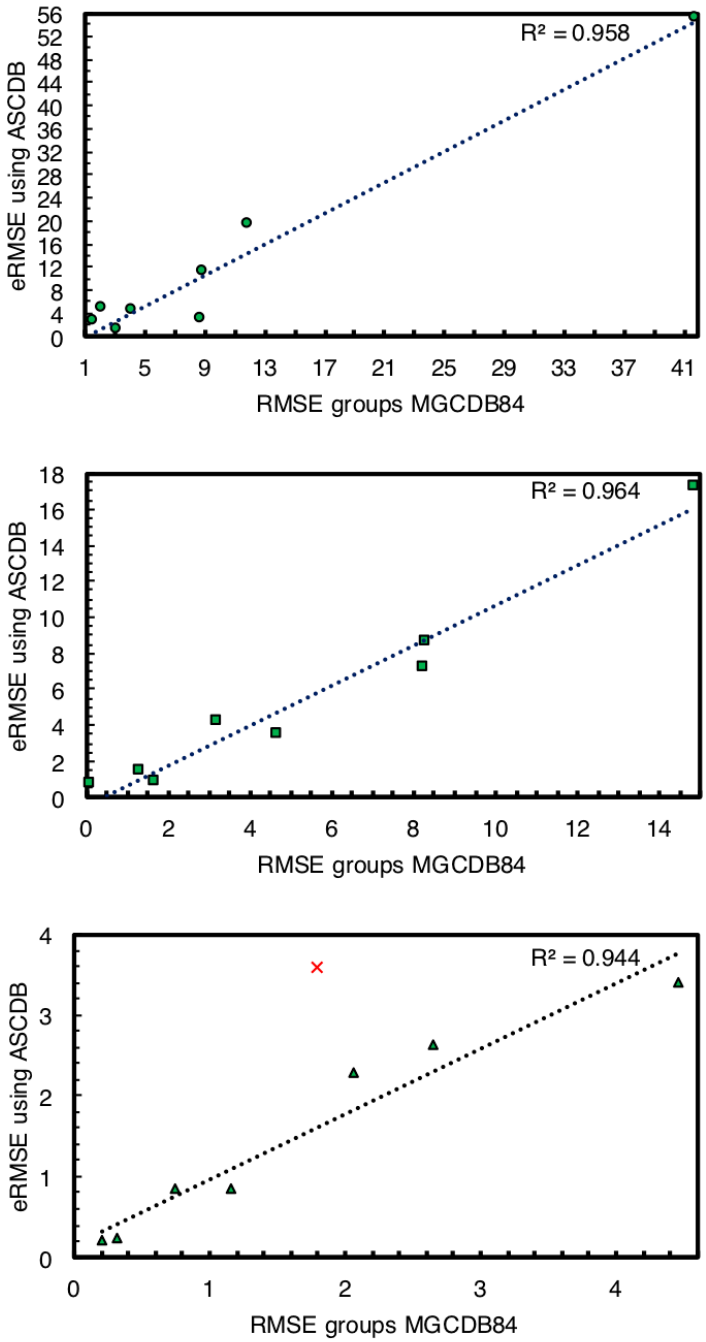

Figure S3 Calculated MUEs plotted against estimated MUEs (eMUEs) for the ωB97M-V functional with three basis sets: 6-31G* (green dots), def2-SVPD (green squares), and def2-TZVPPD (green triangles). The red x indicates the outlier not included in the linear regression. Units on the axis are kcal/mol.

Table S12 Mean Unsigned Errors (MUEs) calculated for two doubly hybrids with the ASCDB (yellow background) and GMTKN55 (red background) databases. All data are in kcal/mol. See also **Figure 4** in the main text. These data complement **Table 3** in the main text.

Subsets	DSD-PBEP86-D3(BJ)	B2PLYP-D3(BJ)	Subsets	DSD-PBEP86-D3(BJ)	B2PLYP-D3(BJ)
NC: A	0.20	0.24	TC: Barrier Heights B	3.38	7.02
Intramolecular NC	0.22	0.23	BHDIV10	1.71	2.13
NC: B	1.16	1.31	NLE: Mixed A	7.5	3.9
Intermolecular NC	0.50	0.45	W4-11MR	6.55	3.04
Non-Covalent: Water	6.34	6.1	NLE: Mixed B	4.54	2.09
WATER27	2.26	2.03	G21EA	1.50	1.29
TC: Atomization and Reaction energies	3.48	2.44	NLE: SIE	3.54	9.16
W4-11nonMR	2.23	1.84	SIE4x4	5.04	10.08
TC: Barrier Heights A	1.61	1.96	UC	5.05	9.79
BH76	1.28	2.59	MB16-43	6.46	16.62

NC stands for Non-Covalent, TC stands for ThermoChemistry, NLE stands for Non-Local Effects, UC stands for Unbiased Calculations. All data are in kcal/mol.

Problematic cases for Doubly-Hybrids.

B2PLYP-D3(BJ):[152,155]
We experienced convergence issues for the following data-points from the Minnesota 2015B database: IP13-20, 4dAEE5-4, HC7-6, MR-TMD-BE3-1, MR-TMD-BE3-3, DC9-6.
For the MGCDB84 database, we had convergence issues with NBC10-78, NBC10-166, 3B-69-DIM-109, NBPRC-11, 3B-69-TRIM-27, 3B-69-TRIM-47, HNBrBDE18-7, FmH2O10-7, PlatonicTAE6-5, PlatonicTAE6-6, PlatonicIG6-4, PlatonicIG6-6, PlatonicHD6-5, PlatonicHD6-6.

DSD-PBEP86-D3(BJ):[160]
We experienced convergence issues for the following data-points from the Minnesota 2015B database: IP13-20, 4dAEE5-4, HC7-6, MR-TMD-BE3-1, MR-TMD-BE3-2, MR-TMD-BE3-3, SR-TM-BE17-7, DC9-6.
For the MGCDB84 database, we had convergence issues with NBC10-78, 3B-69-DIM-109, NBPRC-11, 3B-69-TRIM-27, 3B-69-TRIM-47, HNBrBDE18-7, FmH2O10-7, PlatonicTAE6-5, PlatonicTAE6-6, PlatonicIG6-4, PlatonicIG6-6, PlatonicHD6-5, PlatonicHD6-6.

Table S13 Root Mean-Signed Errors used to generate the plots in **Figure 5** in the main text. All values are in kcal/mol.

Functionals	ASCDB RMSE	MGCDB84 RMSE	GMTKN55 RMSE	Minnesota 2015B RMSE
B3LYP[72-76]	27.72	5.15	12.01	9.03
B3PW91[73,78-80]	18.71	4.66	7.68	8.14
B97-1[82]	16.96	3.6	7.67	5.54
B97-2[83]	20.30	5.07	9.24	6.75
B97-D3(0)[65,66]	24.17	4.4	10.7	10.15
BLYP[73,74]	33.30	7.47	14.77	10.71
BMK[87]	15.53	3.96	4.41	10.37
BP86[73,78]	22.44	6.86	10.17	10.16
HCTH/407[96]	30.78	6.89	12.67	13.12
HSE-HJS[92,98,99]	16.52	4.51	5.67	11.24
M05[103]	14.98	4.08	6.19	7.1
M05-2X[102]	20.26	2.97	6.19	11.59
M06[104]	17.08	3.14	7.54	5.1
M06-2X[104]	18.47	2.54	4.58	11.46
M06-L[106]	40.69	4.49	12.27	6.02
M08-HX[107]	20.53	2.67	4.48	12.93
M11[109]	19.02	3.03	5.75	10.32
M11-L[110]	24.19	4.97	10.93	7.72
MN12-L[116]	15.17	4.25	6.01	8.81
MN12-SX[117]	14.11	4.12	4.66	6.95
MN15[118]	11.29	2.66	4.83	4.38
MN15-L[119]	14.26	4.46	6.15	4.12
N12[121]	15.07	5.27	7.27	8.7
N12-SX[117]	12.63	3.74	5.66	6.37
OLYP[74,122]	35.28	10.18	15.81	10.56
PBE[92]	21.12	7.09	9.47	14.1
PBE0[124]	16.60	4.49	5.64	12.17
PW6B95[127]	14.83	8.6	4.61	25.05
PW91[80]	20.54	6.04	9.29	9.15
revPBE[92,128]	28.03	7.91	12.27	10.08
revTPSS[129]	25.10	5.55	11.9	10.38
RPBE[92,131]	29.54	7.91	12.65	10.04
SOGGA11-X[137]	21.69	3.55	8.02	10.3
τ-HCTH[140]	26.94	5.88	12.5	9.9

τ-HCTHh[140]	17.26	3.83	7.94	6.28
TPSS[142]	22.53	5.03	10.72	8.95
TPSSh[143]	21.44	4.5	9.83	8.37
B97M-V[89]	18.07	3.15	8.34	10.36
B97M-rV[88]	17.79	3.14	8.06	10.39
ωB97X-V[148]	12.73	2.27	7.18	10.68
ωB97M-V[145]	12.99	1.6	4.47	11.35
B3LYP-D3(BJ)[67,72-78]	15.64	3.18	6.42	10.71
PBE-D3(BJ)[67,92]	22.89	7.37	9.6	19.62
PBE0-D3(BJ)[67,124]	17.01	4.46	5.33	14.26
PW6B95-D3(BJ)[67,127]	13.38	8.35	3.84	25.9
SCAN-D3(BJ)[134]	14.12	4	6.51	10.56
SVWN5[72.139]	83.06	41.63	29.58	98.29
HF[97]	139.32	46.39	51.45	61.28
revPBE-D3(BJ)[67,92,128]	18.86	4.58	8.3	11.91
M06-L-D3(0)[66,106]	27.35	4.44	12.16	12.62

Table S14 Mean Signed Errors (MSEs) used for **Figure 6** in the main text. All data are in kcal/mol. We can see sign agreement in all cases except for the revPBE and PBE functionals within the NL and MR-TMD-BE3 subsets.

Functionals	NC ASCDB	NC GMTKN55	NC MGCDB84	NC87 MINNESOTA 2015B	NL ASCDB	MR-TMD-BE3 Minnesota 2015B
HF	-16.58	-2.43	-3.82	-1.58	-79.73	-195.45
OLYP	-8.05	-3.20	-5.43	-4.10	-6.09	-2.98
revPBE	-4.95	-1.92	-3.67	-2.73	-3.43	1.53
RPBE	-4.79	-1.78	-3.35	-2.56	-2.20	2.34
B3PW91	-3.23	-1.45	-2.84	-2.08	-6.12	-52.56
BLYP	-2.74	-0.86	-3.12	-2.33	-12.84	-21.61
B3LYP	-2.21	-1.11	-2.32	-1.80	-10.61	-49.14
PBE	-0.55	-0.31	-1.24	-0.97	10.87	12.80
PBE-D3(BJ)	2.60	0.66	0.50	1.13	14.94	14.73
SVWN5	12.95	2.76	3.15	2.24	51.60	46.87
NC stands for Non-Covalent, NL stands for Non-Local Effects.						

Correlation plots for Chan's MG8 and Gould's dietGMTKN55.

In this section, we want to briefly discuss similarities and differences among the ASCDB, MG8,[177] and dietGMTKN55[178] databases. The correlation plots that we report here (**figures S4** and **S5**) show the good relationship between the mean unsigned errors (MUEs) and the root-mean-square errors (RMSEs) obtained using MG8 and dietGMTKN55-150 and the MUEs and RMSEs of the respective parent databases. We took the dietGMTKN55-150 size because it is the closest to our database, since it has 336 structures. The correlation plots (not reported) for the dietGMTKN55-30 and dietGMTKN55-100 are similar to those reported in **Figure S5**.

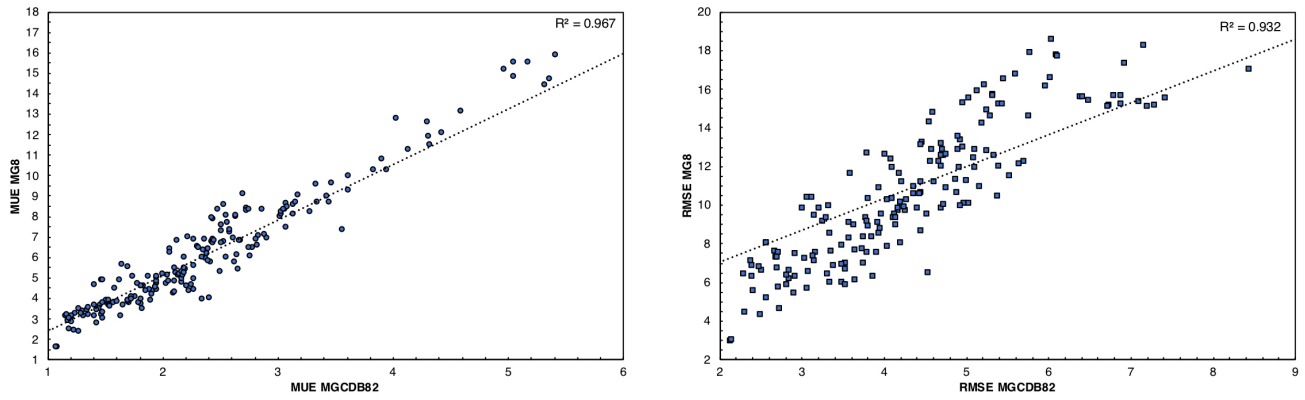

Figure S4 Correlation plots between the mean unsigned errors (MUEs, left pane) and the root-mean-square errors (RMSEs, right pane) calculated using the MG8 and MGCDB82 databases. Units on the axes are kcal/mol.

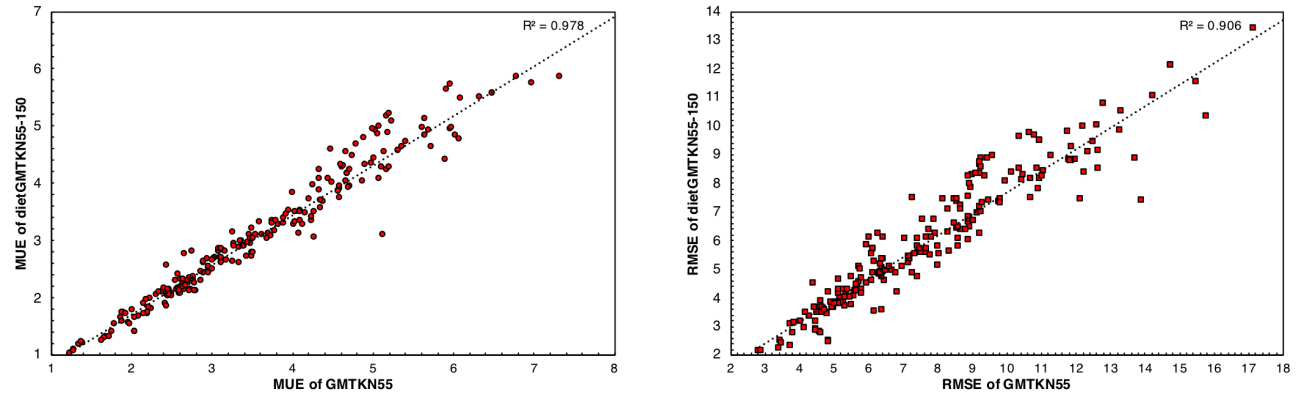

Figure S5 Correlation plots between the mean unsigned errors (MUEs, left pane) and the root-mean-square errors (RMSEs, right pane) calculated using the dietGMTKN55-150 and GMTKN55 databases. Units on the axes are kcal/mol.

It is remarkable that the two databases have a good correlation also for the RMSEs, since this statistical parameter was not considered in their definition. This shows the validity and robustness of the statistical approach, and it is a nice validation not only of Chan's and Gould's works, but also of our own.

However, MG8 and the dietGMTKN55 series are still affected by the same biases that affect their parent databases. As briefly discussed in the main text, neither of them includes transition metals, which should be mandatory in a modern database for functional parameterization, and this probably constitutes their most notable limitation. Furthermore, they do not include atomic energies: the GMTKN55 database does not include atomic energies, and so does dietGMTKN55, while Chan excluded a priori the significance of atomic energies (and noble gas dimers). As we see in the main text, once the three databases are put together, atomic energies *are* statistically significant. When it comes to size, though, our database is the largest since it has 350 single-point (SP) calculations. The smallest is the dietGMTKN55-30 database, with only 82 SP calculations, followed by MG8 (140 SP calculations), dietGMTKN55-100 (238 SP calculations), and dietGMTKN55-150 (336 SP calculations). However, this is not reflected in the computational time: using the HF method and the 3-21G basis set on a recently purchased machine with the Q-Chem code, ASCDB outperformed all the databases except the smallest one when it comes to single-core performance.

Each one of the resulting databases is well balanced with respect to the size of the molecules under discussion: we already pointed out that molecules with more than 30 atoms represent 6% of ASCDB. Here we stress that they represent about 9% of MG8, 6% of dietGMTKN55-30, and 8% for both dietGMTKN55-100 and dietGMTKN55-150. However, the other databases are not balanced with respect to the number of data-points per chemical property. Taking dietGMTKN55-150 as an example, non-covalent interactions represent 42% of the data-points, while basic properties (which can be roughly be compared with our ThermoChemistry subset) represent 33% of the data-base. Reaction Energies represent only 11%, while Barrier Heights represent 15%. In general, the whole dietGMTKN55 series is unbalanced towards non-covalent interactions. The same is true for MG8 as well: in fact, 26 data-points out of 64 (42%) describe non-covalent interactions, isomerization energies represent 34% of the database, thermochemistry and barrier heights only 14% and 11% respectively. Everything we said so far is summarized in **table S15**.

Database	Reliable?	Transition metals?	Atomic Energies?	Size (# of structures)	Computational time (s)	Balanced?
MG8	✓	✗	✗	140	723	✗
dietGMTKN55-30	✓	✗	✗	82	150	✗
dietGMTKN55-100	✓	✗	✗	238	837	✗
dietGMTKN55-150	✓	✗	✗	336	2772	✗
ASCDB	✓	✓	✓	350	537	✓

Table S15 Visual summary of the properties of the three small databases MG8, dietGMTKN55, and ASCDB.

In conclusion, it is up to the user to choose the database that most fits their preferences. If one looks for a small database that it is significant and reliable, then each one of the five described above is a good choice. However, we recommend our ASCDB because it covers a broader spectrum of molecules, going from atoms to large molecules, including transition metals and transition-metal systems, and conveys information from three parent databases, not just one. All of it is done a well-balanced fashion, with each chemical property well represented, and it is not computationally demanding, as shown by the single-core performance using HF/3-21G as test method.

References.

Basis sets (page S2).

We refer the reader to the website https://comp.chem.umn.edu/basissets/basis.cgi for more information about the basis sets developed (and used) by the Truhlar group, together with the Supporting Information of Ref. 62-64. We refer the reader to the website http://tyr0.chem.wsu.edu/~kipeters/pages/cc_append.html for more information about the Dunning's basis sets (last access on February 7th 2019)

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